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# MECHANISM GOVERNING THE SENSITIVITY OF A THREE-ELECTRODE IONIZATION CHAMBER

E. B. SHMIDEL* and L. I. KALABINA
*All-Union Research, Development and Design Institute of Chromatography, N. Syromiatnicheskaia 5/7, Moscow 107120 (U.S.S.R.)*

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## SUMMARY

A mechanism is proposed for describing the sensitivity of a three-electrode ionization chamber powered by an alternating current. The useful signal is shown to be shaped by variations in charge-carrier mobility due to the presence of the substance under test in the sensitive volume while recombination effects are not the determining factor. Variations of carrier mobility induce changes in the measuring electrode voltage, this finally leading to an avalanche-like current variation.

The functional relationships between the measuring electrode current, the charge carrier characteristics and the power supply mode lead to the conclusion that, with an adequate number of charge-carrier types, it is possible to register certain ion–molecule interactions and changes in the detection selectivity. The mechanism described is not claimed to be exhaustive and is presented for further discussion.

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## INTRODUCTION

Ionization techniques occupy a particular place among physical and physicochemical methods of gas analysis, featuring high sensitivity and simplicity of hardware construction, but their comparatively low selectivity is a major drawback. The operation of ionization techniques is based on interactions between ions and molecules, between excited carrier gas atoms and the substance under analysis, and interactions of, *e.g.*, radioactive emission, with the carrier gas and substance under analysis. Most often, these processes are carried out in an inert carrier gas, with two types of charge carriers generated under the effects of radioactive emission, *viz.*, electrons and positive ions. Therefore, the types of substance interactions, which determine the selectivity of the method, are restricted. When air is used as the carrier gas, the following charge carriers are generated: an electron, a positive nitrogen ion, a negative oxygen ion, a positive oxygen ion and various compounds with water, such as $(H_2O)_nO_2$, and with positive ions. As is well known, the value of $n$ here is a function of moisture concentration and gas temperature[1].

It appears very promising to use various cross-sections of interactions between the substance being analysed and various charge carriers and to measure the specific effect of interactions on detection sensitivity and selectivity.

Smith and Merrit[2] described a three-electrode a.c. ionization chamber. Currently, a gas chromatograph with a three-electrode a.c.-excited ionization chamber as the detector is manufactured in the U.S.S.R. The detector is termed ionization-resonant (IRD) and is of coaxial design, in which the middle electrode is a cylindrical bar and the potential electrodes are two parts of a cylinder insulated from one another. This detector is used to detect substances with a positive affinity for electrons in nitrogen. Its sensitivity to such substances is of the same level as that of the widely described electron-capture detector. This has led to the conclusion that the mechanisms in both are identical, *i.e.*, the sensitivity is considered to be governed by recombination effects[3-5].

The above conclusion can easily be shown to be unjustified. Current losses due to recombination and diffusion during ion acquisition can be calculated in terms of the maximal saturation current under resonance conditions[6]:

$$\frac{\Delta I}{I} = \frac{\beta n_0 (b - a)^2}{6 V^+ V^-} \tag{1}$$

where $\beta$ is the recombination factor, $n_0$ is the number of ion pairs generated by the emission per second, $b - a$ is the distance between the electrodes where $b$ and $a$ are the outer and inner electrode radius, respectively, and $V^+$ and $V^-$ are the velocities of positive and negative anion drifts, respectively. For nitrogen, $\beta = 10^{-9}$ cm$^3$/s; for air, $\beta = 1.5 \cdot 10^{-6}$ cm$^3$/s[7]. Taking into account the activity of the ionizing source, about $10^{10}$ ions per second are generated in the detector volume.

The ion drift velocity may be calculated from the average field intensity in the inter-electrode gap of a coaxial IRD to account for the non-uniformity of this field; such an approximation will not affect the end result significantly.

At normal pressure, the average ion velocity is

$$V_{av} = \mu E_{av} \tag{2}$$

where $\mu$ is the mobility of carrier gas ions and

$$E_{av} = \frac{U(a + b)}{2\, ab \ln (b/a)} \tag{3}$$

where $U$ is the voltage across the electrodes. For nitrogen, $\mu_+ = 1.8$ and $\mu_- = 10^3$; for air, $\mu_+ = 1.8$ and $\mu_- = 2.5$[8].

Hence, the loss of current due to recombination and diffusion will be 5.5% in nitrogen and 1.15% in air. These losses are negligible, this being an indication of the detector operating under saturation conditions. As is well known, recombination effects are realized on the mobility section of the $V/A$ characteristic (Ohm's law), which is positioned at 0.7–0.8 of the saturation current.

## IRD SENSITIVITY MECHANISM

It is very important to establish the mechanism governing IRD sensitivity (*i.e.*, shaping of the useful signal) and show the feasibility of the control of its selectivity by registering various interactions of a substance under analysis with the carrier gas ions. In the general case, the current through the chamber may be described by the following system of equations:

$$\begin{aligned} &\operatorname{div} E = \rho/\varepsilon_0 \\ &\operatorname{div} j = 0 \\ &j = j_c + j_d = \rho\mu E + D \operatorname{grad} \rho \end{aligned} \qquad (4)$$

where $E$ is the field intensity, $\rho$ is the charge density, $\varepsilon_0$ is the permittivity of vacuum ($8.855 \cdot 10^{-12}$ F/m), $j_d$ and $j_c$ are the diffusion and convection current densities, respectively, and $D$ is the diffusion factor.

From this system of equations, it follows that

$$D \operatorname{div} \operatorname{grad} \rho + \mu E \operatorname{grad} \rho + \mu\rho^2/\varepsilon_0 = 0 \qquad (5)$$

In a rectangular system of coordinates, this can be rewritten as

$$D\left(\frac{\partial^2\rho}{\partial x^2} + \frac{\partial^2\rho}{\partial y^2}\right) + \mu(E_x \cdot \frac{\partial\rho}{\partial x} + \mathrm{E}_y \cdot \frac{\partial\rho}{\partial y}) + \mu\rho^2/\varepsilon_0 = 0 \qquad (6)$$

and if the smallness of current due to diffusion ($D = 0$) is taken into account, the measuring electrode current can be written as

$$I = \int_s \rho\mu E \mathrm{d}S \qquad (7)$$

where $S$ is the current-carrying surface area of the measuring electrode. If the charge density along the measuring electrode is assumed to be constant, then

$$\frac{\partial\rho}{\partial l} = \frac{\rho^2}{\varepsilon_0 E} \qquad (8)$$

where $l$ is the electrode length; application of eqn. 7 gives the measuring electrode current:

$$I = I_0\,[m(\arccos m - \pi) - (l - m^2)^{1/2}] \qquad (9)$$

where $I_0 = 4\,a\rho\mu E$, $m = q/4\pi a\varepsilon_0 E$, $-1 < m < +1$, $q$ is the measuring electrode charge, arc cos $m$ is for angles $\alpha_1$ and $\alpha_2$ ($\alpha$ is the angle between the $E_0$ and $E$ vectors, $0 < \alpha < \pi/2$), and $E_0$ is the horizontal field intensity.

When $-1 < m < +1$ the space which is the drain space for ions of one polarity will be the shadow space for ions of opposite polarity. The measuring electrode will gather ions of both polarities and, therefore, its total current will be the sum of positive and negative ion currents:

$$I = I_+ + I_- \qquad (10)$$

where $I_+$ and $I_-$ are the positive and negative ion currents, respectively.

The total field intensity at the surface of a cylindrical electrode is

$$E = 2E_0 (\cos \alpha - m) \tag{11}$$

Hence, it follows that at $m > 1$ the field intensity retains its polarity along the entire measuring electrode surface and is directed towards the centre of the electrode. Therefore, the measuring electrode collects only positive ions on its entire surface. At $m < 1$ the field intensity at the entire electrode surface is directed from the electrode, and ions do not arrive at the electrode in their entirety, but rather flow around it. Therefore, variations of the value of $m$ within certain limits can be used to collect ions of one polarity or both polarities or to exclude ion acquisition totally.

According to the Ramo–Shockley theorem[9], ions induce a charge on the electrode, this charge increasing as ions come nearer to the electrode surface:

$$q = en\int_0^t VE_v \mathrm{d}t \tag{12}$$

where $e$ is the electron charge, $n$ is the number of travelling ions and $E_v$ is the field intensity at a point where the difference between electrode potentials is 1 V at a given moment of time.

For an a.c.-powered coaxial chamber (*e.g.*, with a sinusoidal current), it may be stated that

$$V = \mu E_{av} \tag{13}$$

$$V = \frac{\mu u_0 \sin\omega t(a + b)}{2ab\ln(b/a)}$$

where $u_0$ is the a.c. voltage amplitude and $\omega$ is the angular frequency, $t = \pi/\omega$. If, during a half-period, ions are displaced by less than the spacing between the electrodes, then a displacement current is generated; if, during the same time, ions move to distances equal to or greater than the spacing between the electrodes, then a conductivity current is generated.

After transforms, the Ramo–Shockley equation can be rewritten as

$$q = \frac{en\mu u_0(a + b)^2}{2\omega(ab\ln(b/a))^2} \tag{14}$$

As is evident from eqn. 14, the value of the measuring electrode charge is determined by the charge-carrier concentration and mobility, the voltage and frequency of the power supply and the dimensions of and spacing between the electrodes. Obviously, a combination of these parameters may be selected to ensure the arrival of ions of a certain polarity or complexes at the measuring electrode.

Resonance conditions correspond to the maximal conductivity current and can be determined from

$$X = b - a \tag{15}$$

where $X$ is the ion displacement during a voltage half-wave:

$$X = \int_0^{\frac{\pi}{\omega}} \mu E(t)\mathrm{d}t \tag{16}$$

and $E(t)$ is the instantaneous field intensity at the ion site under a.c. power, $E(t) = E_{av}$. Taking eqn. 15 into account results in

$$\frac{\mu u_0(a + b)^2}{\omega ab\ln(b/a)} = b - a \quad \text{or} \quad \frac{u_0}{f} = \frac{2\pi ab\ln(b/a)\,(b-a)}{\mu(a + b)^2} \tag{17}$$

where $\omega = 2\pi f$. This describes resonance conditions for the collection of ions of a certain mobility.

The magnitude and polarity of charge $q$ determine the value of $m$, and hence the measuring electrode field intensity. The magnitude of $q$ can easily be determined for the collection of ions of various mobilities and different polarities under conditions of uniform gas ionization in the sensitive volume of the chamber:

$$q = q_- + q_+; \quad q = \frac{enu_0(a + b)^2}{2f[ab\ln(b/a)]^2} \cdot (\mu_2 - \mu_1) \tag{18}$$

Hence, the initial current differs from zero if $\mu_1 \neq \mu_2$. On the other hand, $q$ can acquire almost any magnitude, depending on the frequency of the supply voltage. This can be taken to indicate the possibility of selecting a suitable operating mode for an IRD.

It is now expedient to discuss the mechanism of useful signal generation in an IRD; to this end, consider the measurement circuit in Fig. 1 and the equivalent circuit in Fig. 2. Treating these circuit arrangements by the partial capacitances technique and taking account of the inter-electrode capacitances between the measuring (middle) and potential (extreme) electrodes and the mid-point (ground), it can easily be shown that the potential of the measuring electrode relative to the mid-point, $\Delta\varphi$, can be calculated in terms of the set-point potential, $\varphi_0$, as

$$\Delta\varphi = \varphi_0 C_3/(C_3 + C_4) \tag{19}$$

On the other hand, $\Delta\varphi$ varies with changing $C_4$ at a constant $C_3$ and, therefore, with a potential of the measuring electrode that is adequate to collect ions of certain kinds, $C_4$ acquires a steady-state value and the collected ions generate a conductivity current. However, if ion-molecule interactions change the ion mobility (*e.g.*, cause a lower mobility), then ions generate a displacement current, thus increasing $C_4$ and

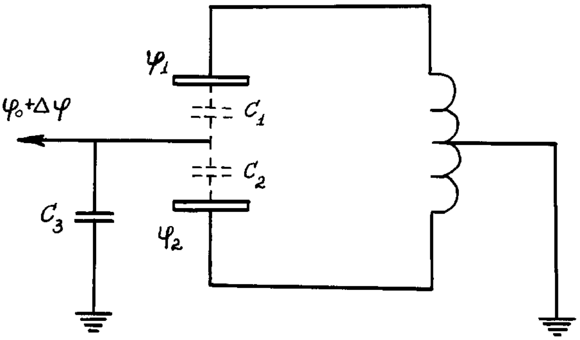

Fig. 1. IRD measurement circuit. $C_1$, Inter-electrode capacitance between the measuring electrode and one of the potential electrodes; $C_2$, inter-electrode capacitance between the measuring electrode and the other potential electrode; $\varphi_1$, $\varphi_2$, potentials of the first and second potential electrodes relative to power supply mid-point (ground); $\varphi_0 + \Delta\varphi$, potential of the measuring electrode relative to the supply mid-point; $C_3$, capacitance of the measuring electrode relative to the power supply mid-point.

decreasing $\Delta\varphi$ in an avalanche-like manner. As is evident from eqn. 19, $\Delta\varphi$ varies (decreases) not only due to ions interacting with molecules of the substance under analysis, but also due to carrier gas ions generating a displacement current at a reduced potential of the measuring electrode, this in turn changing (increasing) $C_4$. This explains the high sensitivity of IRD to variations of charge-carrier mobility. In other words, useful signal generation is based on avalanche-like variations of the measuring electrode potential, caused by charge-carrier mobility changes in the sensitive volume, these changes being due to various interactions with the substance being analysed. Hence the possibility of controlling IRD selectivity has been demonstrated and the mechanism of useful signal generation has been determined.

The mechanism described provides unique requirements for IRD design; in particular, a most important condition for realizing this mechanism is a short ion-

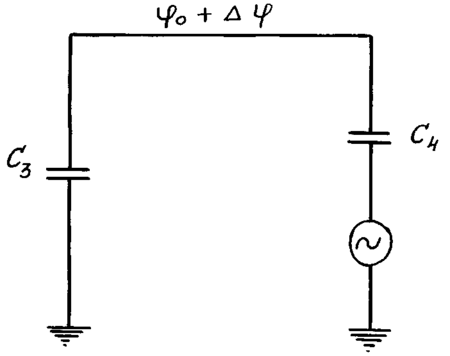

Fig. 2. IRD equivalent measurement circuit. $\varphi_0 + \Delta\varphi$, Potentials of the measuring electrode relative to the supply mid-point; $C_3$, capacitance of the measuring electrode relative to the power supply mid-point; $C_4 = C_1 + C_2$; $C_1$, inter-electrode capacitance between the measuring electrode and one of the potential electrodes; $C_2$, inter-electrode capacitance between the measuring electrode and the other potential electrode.

ization zone in the inter-electrode gap, *i.e.*, the ionization zone should be significantly less than the spacing between the measuring and potential electrodes (potential electrodes function as ionization sources). It should be noted that the mechanism described is not claimed to be complete but is the first attempt to explain signal generation in three-electrode a.c. ionization chambers.

It will be useful to relate the current magnitude to the concentration of the substance under analysis. Extracting $\rho\mu$ from the integral in eqn. 17 and applying the Gauss theorem, we obtain

$$I = \rho\mu q/\varepsilon_0 \tag{20}$$

It may be assumed that

$$q = C_3(u - u_0) = C_3\Delta u \quad \text{and} \quad \Delta u = \Delta\varphi \tag{21}$$

and taking eqns. 20 and 21 into account,

$$I = \frac{\rho\mu C_3\varphi_0 C_3/(C_3 + C_4)}{\varepsilon_0} \tag{22}$$

Variations of permittivity in an IRD will produce changes in $C_4$ in accordance with

$$\Delta C_4 = C_4\Delta\varepsilon \tag{23}$$

To relate the measurement electrode current to variations in charge carrier mobility, we shall use the mobility equation[10] with the following assumptions: (1) gas molecules are under the effect of polarization attraction to the change; (2) ion velocities comply with Maxwell's distribution; and (3) the directional velocity of ions is small compared with the thermal velocity (about 100 times less). Therefore,

$$\mu = \frac{0.235}{(\rho/\rho_0)\sqrt{(\varepsilon - 1)\, M_0}} \cdot \sqrt{\frac{m_\mathrm{m} + m_\mathrm{i}}{m_\mathrm{i}}} \tag{24}$$

where $\rho_0$ is the current density under normal conditions, $M_0$ is the molecular weight of the gas, $m_\mathrm{m}$ is the mass of the molecule, $m_\mathrm{i}$ is the mass of the ion and $\varepsilon$ is the carrier gas permittivity. The mass of the ion and molecule can be assumed to be equal (in the present instance this does not introduce a noticeable error) and $\rho = \rho_0$; with these assumptions, eqn. 24 is reduced to

$$\mu = \frac{0.235\sqrt{2}}{\sqrt{(\varepsilon - 1)\, M_0}} \tag{25}$$

Hence

$$\varepsilon = \frac{0.11 + \mu^2 M_0}{M_0\mu^2} \tag{26}$$

$$\Delta\varepsilon = \varepsilon_{\text{mix}} - \varepsilon \tag{27}$$

where $\varepsilon_{\text{mix}}$ is the permittivity of the carrier gas with an admixture;

$$\Delta\varepsilon = \frac{0.11 + \mu_{\text{mix}}^2 M_0}{M_0 \mu_{\text{mix}}^2} - \frac{0.11 + \mu^2 M_0}{M_0 \mu^2} \tag{28}$$

where $\mu_{\text{mix}}$ is the ion mobility in the carrier gas with an admixture. After transformation,

$$\Delta\varepsilon = k_1 \left( \frac{1}{\mu_{\text{mix}}^2} - \frac{1}{\mu^2} \right); \quad k_1 = 0.11/M_0 \tag{29}$$

As is well known[11],

$$\mu_{\text{mix}} = \frac{\mu \mu_{\text{ad}}}{c\mu + (1 - c)\mu_{\text{ad}}} \tag{30}$$

where $\mu_{\text{ad}}$ is the admixture ion mobility. If $c$ is the concentration of admixture,

$$\Delta\varepsilon = k_1 \left( \frac{c^2}{\mu_{\text{ad}}^2} + \frac{2c}{\mu \mu_{\text{ad}}} \right) \tag{31}$$

Actual data show that the term $c^2/\mu_{\text{ad}}^2$ is negligible ($c = 10^{-8}\%$), and therefore

$$\Delta\varepsilon = 2k_1 c/\mu \mu_{\text{ad}} \tag{32}$$

The current variations due to changes in charge mobility, caused by the presence of the admixture in the sensitive volume, are

$$\Delta I = I - I_{\text{mix}} \tag{33}$$

where $I$ is the current during carrier gas transfer and $I_{\text{mix}}$ is the current when carrier gas with the admixture is transferred through the volume:

$$\Delta I = -\frac{k_2 C_4 \Delta\varepsilon}{k_3^2 + k_3 C_4 \Delta\varepsilon} \tag{34}$$

Substituting $\Delta\varepsilon$ and performing some manipulations, we arrive at the final equation for current variations due to charge mobility, changes caused by the presence of the admixture in the sensitive volume:

$$\Delta I = -\frac{k_4}{\dfrac{k_3^2 \mu \mu_{\text{ad}}}{c} + k_5} \tag{35}$$

where $k_1 = 0.11/M_0$, $k_2 = \rho\mu C_3\varphi_0/\varepsilon_0$, $k_3 = C_3 + C_4$, $k_4 = k_2C_42k_1$ and $k_5 = k_3C_42k_1$. The minus sign indicates a current decrease. However, an increase in the magnitude of the current is not ruled out.

The equations derived do not take into account the mobility of ions generated by interaction of the substance under analysis with carrier gas ions; this significantly impairs the accuracy of eqn. 35. However, when discussing the analysis of a specific substance with known ion–molecule interactions, the equation arrived at can be made more accurate by replacing the admixture ion mobility with the mobility of generated ions or their complexes with the carrier gas.

## CONCLUSIONS

Some insight has been obtained into the mechanism governing the sensitivity of a three-electrode a.c. ionization chamber. The possibility of controlling the detection selectivity has been demonstrated. The functional relationships presented indicate the potential fields of application of this method for solving analytical problems.

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